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RATIO OF SEVEN- TO SIX-MEMBERED RING SULFONES IN THE CYCLIZATION OF A SULFONYL CARBENE

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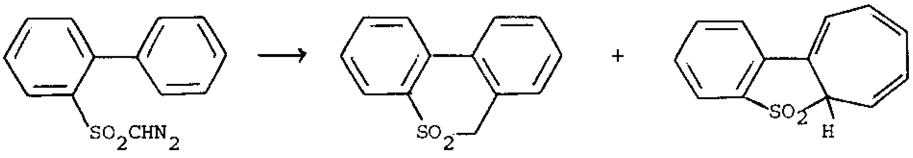
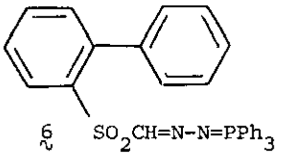
The ratio of 7- to 6-membered ring intramolecular cyclization product increases with decreasing solvent polarity in the $(C_6F_5Cu)_4$ catalyzed decomposition of **1** and with increasing temperature in the uncatalyzed decompositions. Possible explanations are discussed.

To account for the dependence of the ratio of **3**:**2** upon solvent polarity in the thermolysis of biphenyl-2-sulfonyldiazomethane (**1**) we proposed a transition state **4** in which bond formation between the carbene and the two ring carbon atoms had proceeded to different extents.[1] We now report the effect of solvent polarity on the catalyzed low temperature decomposition of **1** and a striking temperature effect on the **3**:**2** ratio from the free carbene, which shed further light upon the mechanism of the intramolecular cyclization.

Smooth decomposition of **1** at room temperature was achieved using catalytic amounts of $(C_6F_5Cu)_4$. Change in the solvent polarity ($CHCl_3$ - C_6H_{12}) has a marked effect upon the **3**:**2** ratio. As the weight % of the non-polar solvent increases from 0 to 100% in the mixture the **3**:**2** ratio changes from 1.6 to 5.8. The total yield **3** + **2** remains relatively constant (53-58%). This is not only a mechanistically, but also a preparatively, useful observation. No intermolecular insertion into solvent by the carbenoid intermediate was observed; the ethylene **5** was obtained, but its formation was completely suppressed by the addition of piperylene,[2] while the **3**:**2** ratio was unchanged in the presence of piperylene. This confirms that dimer **5** probably arises from the triplet,[3] and supports an unsymmetrical transition state leading to **2**.



1 **2** **3**



6

+ $ArSO_2CH=CHSO_2Ar$

5

The triphenylphosphazene (**6**),[4] mp 173°, was prepared from **1** and Ph_3P and was used as a source[5] of the sulfonylcarbene at temperatures above the normal decomposition temperature of **1**. This permitted a study of the variation in the **3**:**2** ratio from **3** in cyclohexane between 135-180° (Table). Appreciable amounts of cyclohexane insertion product (**7**) were obtained as well.

TABLE Variation with temperature in product ratio from **6**

Temp. (°C)	Reaction time (min)	% Yields **2**	**3**	**7**	(**2**+**3**+**7**)	(**2**+**3**)/**7**	**3**:**2**
135	600	6.9	31.6	17.0	55.5	2.3	4.6
150	120	6.1	37.3	16.0	59.4	2.7	6.1
160	30	5.7	42.4	15.2	63.3	3.2	7.4
170	20	5.8	45.0	15.8	66.6	3.2	7.7
180	10	6.0	50.0	15.8	71.8	3.5	8.4

It is clear that, with increasing temperature, the absolute yields of 2 and 7 remain approximately constant but that of 3 increases appreciably. Alternatively, the *relative* yield of 3 may be viewed as going up from 56.9 to 69.6% while those of 2 and 7 go down from 12.4 to 8.4% and 30.6 to 22.0%, respectively. The ratio of seven- to six-membered ring cyclization product almost doubles with a 45° increase in temperature.[6] Both 2 and 3 are stable under the reaction conditions and at 180° in the presence of Ph_3P. Unlike *N*-sulfonylazepines[7] 3 does not rearrange thermally to 2 at 300° for 1 hr. and the absence of this $2 \rightleftharpoons 3$ interconversion provides a key to possible explanations of the results.

Of these, two can be retained for further discussion. The dimer and sulfonate ester[1] are products of triplet carbene reactions. The intermolecular insertion product into cyclohexane (7) and intramolecular cyclization products are singlet carbene (or carbenoid in the catalyzed decompositions) products. To account for the temperature effect one could postulate that two different singlet carbene states are involved: the cyclohexane insertion (5) and six-membered cyclization (2) products could arise from an S_0 state, while the cycloheptatriene (3) could arise from an S_1 carbene (or thermally excited linear S_0 carbene) *via* a norcaradiene intermediate. S_0 carbenes are thought to add *via* an unsymmetrical transition state to olefinic double bonds;[8] this would be similar to our previously postulated[1] T.S. 4 which could readily open up to 2 *via* the dipolar σ-complex. On the other hand, S_1 or linear S_0 methylene is predicted to add *via* a symmetric T.S. to ethylene,[9] and such a T.S. would transform smoothly either to the norcaradiene intermediate or directly, in a concerted bond-forming ring-expansion process, to the cycloheptatriene (3), a process that would be favoured by entropy considerations. Raising the temperature would increase the population of S_1 carbene[10] and hence 3 relative to 2.[14]

A simpler explanation would be that **2**,**3** and **7** all arise from the S_0 singlet carbene by competing intra- and intermolecular pathways. Formation of **3** would be favoured at the higher temperatures, provided **2** and **3** were formed *irreversibly* (**2** ⇄ **3** does not obtain as shown earlier) from a common norcaradiene intermediate (**8**), and $\Delta H^{\dagger}_{3}$ is higher that $\Delta H^{\dagger}_{2}$.[15] This is depicted in the Scheme. Preliminary results[1,17] with the 4'-bromo- and 4'-nitro-derivatives of **1** support the above conclusions.

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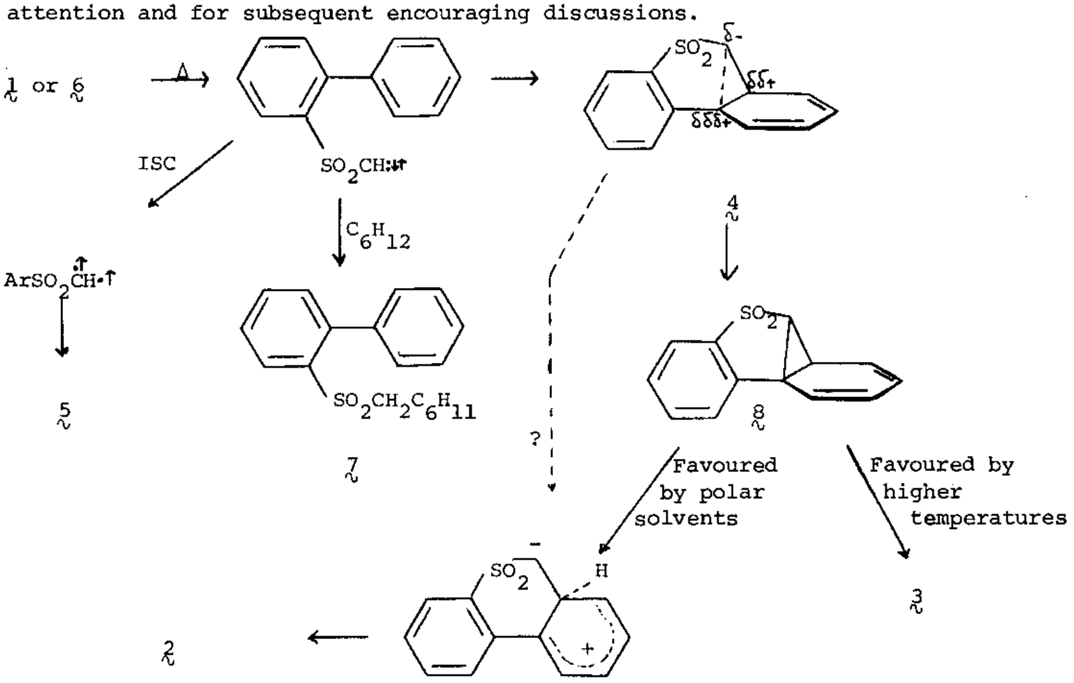


SCHEME

1. R. A. Abramovitch, V. Alexanian, and E. M. Smith, *J. C. S. Chem. Comm.*, 893 (1972).

2. R. A. Moss, in "Carbenes," M. Jones, Jr. and R. A. Moss, ed., Vol. 1, John Wiley and Sons, New York, 1973, p. 283.

3. J. V. Gramas, *Diss. Abstr.*, **26**, 4235 (1966).

4. Gave the correct analytical and spectral data.

5. D. R. Dalton and S. A. Liebman, *Tetrahedron*, **25**, 3321 (1969).

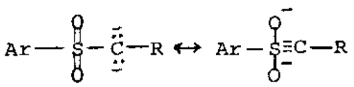
6. The lower overall yields of **2** + **3** + **7** at lower temperatures could be due to a possible competition from phosphorane formation[5] from any solid **6** in suspension. Attempts to isolate such a phosphorane were unsuccessful, however.

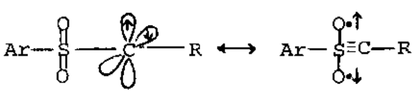
7. R. A. Abramovitch, T. D. Bailey, T. Takaya, and V. Uma, *J. Org. Chem.*, **39**, 340 (1974).

8. R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968). R. Hoffmann, D. M. Hayes, and P. S. Skell, *J. Phys. Chem.*, **76**, 664 (1972).

9. A. G. Anastassiou, *J. C. S. Chem. Comm.*, 991 (1968).

10. The S_1 state of CH_2 lies *ca.* 20 kcal above the S_0 state[11] and *ca.* 10 kcal above the linear S_0 state and its involvement in the 2062 Å photolysis of ketene is suspected.[12] An S_1 sulfonyl carbene may be appreciably stabilized relative to the S_0 state by the same types of interactions proposed[13] to account for the formation of α-sulfonyl dicarbanions:





and might make the S_1 sulfonyl carbene thermally accessible in solution.

11. G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971). M. J. S. Dewar, R. C. Haddon, and P. K. Weiner, *J. Amer. Chem. Soc.*, **96**, 253 (1974).

12. H. M. Frey, G. R. Jackson, M. Thompson, and R. Walsh, *J. C. S. Faraday Trans. I*, 2054 (1973).

13. E. M. Kaiser, L. E. Solter, R. A. Schwarz, R. D. Beard, and C. R. Hauser, *J. Amer. Chem. Soc.*, **93**, 4237 (1971).

14. An argument against an S_1 intermediate could be that one might expect it to be trapped by piperylene in the same way as is the triplet.

15. If such a competitive ring-opening of **8** to **3** and **2** is assumed log ($k_{\mathbf{3}}/k_{\mathbf{2}}$) can be plotted *vs.* 1/T[16] to give $\Delta H^{\dagger}_{\mathbf{3}} - \Delta H^{\dagger}_{\mathbf{2}} = 4.9 \pm 1$ kcal/mole and $\Delta S^{\dagger}_{\mathbf{3}} - \Delta S^{\dagger}_{\mathbf{2}} = 15 \pm 2$ e.u.

16. S. S. Olin and R. M. Venable, *J. C. S. Chem. Comm.*, 104 (1974).

17. R. A. Abramovitch and V. Alexanian, unpublished results.

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